Assessment of the effect of sulphur supplied to the soil with mineral fertilizers and waste from magnesium sulphate production on its content in spring wheat (*Triticum aestivum* L.) and in soil effluents

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Abstract. The assessment of the effect of fertilization on the plant, soil and sulphur losses as a result of leaching was conducted in a pot experiment.

The experiment was conducted in three replications and two series: without liming (0 Ca) and limed (+ Ca) on 6 treatments: 0 - soil without fertilizers, NPK - soil fertilized with nitrogen,phosphorus and potassium, NPK + S1 a.s. - soil fertilized withnitrogen, phosphorus, potassium and sulphur supplied as ammonium sulphate, NPK + S1 w. - soil fertilized with nitrogen,phosphorus, potassium and sulphur supplied with the waste frommagnesium sulphate production and NPK + S3 a.s. - soil fertilized with nitrogen, phosphorus, potassium and sulphur suppliedas ammonium sulphate in a dose three times bigger than introduced to the soil on NPK + S1 a.s. and NPK + S1 w. treatments.Spring wheat was cultivated in each year of the experiment. Thesulphur content in the prepared experimental material (plant, soiland effluent) was assessed by means of ICP-AES method onJY 238 Ultrace apparatus.

An average (over three years) total yield of spring wheat (grains, straw and roots) at comparable values of standard error of arithmetic mean for individual treatments was the highest after sulphur application in the form of ammonium sulphate. In comparison with biomass yields from the treatments where a lower sulphur dose was used, either as ammonium sulphate or the waste from magnesium sulphate production, smaller biomass yield was obtained in the treatment where sulphur was applied in a dose which was thrice as high. Weighed arithmetic mean of the sulphur content in grains, straw and roots of wheat fertilized with sulphur was significantly higher than the content assessed in wheat biomass not fertilized with this element. Increasing sulphur dose did not cause any significant differences in this element content in wheat biomass. A single soil fertilization with smaller sulphur doses either as ammonium sulphate or as waste from magnesium sulphate production did not cause any lasting fertilizer effect, a result of removal of sulphur with the crop and its leaching from soil. Sulphur fertilization, either as ammonium sulphate or as

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waste from magnesium sulphate production led to an increased sulphur content in soil effluents. The amounts of this element in leaching waters were affected mainly by the quantity of sulphur supplied to the soil with fertilization and, to a lesser degree, by the plant yields.

key words: fertilization, sulphur, spring wheat, soil, soil effluents

INTRODUCTION

Sulphur like nitrogen, phosphorus, potassium, magnesium and calcium belongs to nutrient macroelements absorbed by plants in the greatest amounts. Its physiological role is specific and impossible to be replaced by any other element. The unique role of sulphur results from its function in plant metabolism, mainly in the transformation of nitrogen compounds (Schnug, 1998; Ostrowska et al., 2008).

Sulphate anion (SO_4^{2-}) is the basic source of sulphur for plants. The quantity and rate of its uptake depend on many factors, among others on soil reaction, temperature, sulphate content in the soil solution, the content of other ions and also on the soil biological activity (Kertesz and Mirleau, 2004).

High requirements of some plants for sulphur, decreased use of fertilizers containing this element, reduction in emission of sulphur compounds into the atmosphere and considerable sulphate leaching lead to a negative balance of this element in many soils (Schnug, 1998; Zhao et al., 2003; Mathot et al., 2008). Sulphur deficiency in plants may limit utilization of other elements, including nitrogen, which in consequence leads to a decline in yield and worsens crop quality (Luo et al., 2000; Wieser et al., 2004).

Identification of the effect of fertilization with these substances of waste origin on the sulphur content in plant and soil, and determining losses of this element through leaching are important to ensure the optimal level of

Property	Soil	Property	Waste
pH H ₂ O	6.33 ± 0.01	pH H ₂ O	9.53 ± 0.09
pH KCl	5.70 ± 0.02	Dry matter [g kg ⁻¹]	630 ± 31
Hydrolitic acidity [mmol(+) kg ⁻¹ DM]	23.9 ± 1.2	Ash [g kg ⁻¹ DM]	726 ± 37
Organic C [g kg ⁻¹ DM]	19.3 ± 1.1	Total forms [g kg ⁻¹ DM]	
Total N [g kg ⁻¹ DM]	1.60 ± 0.12	Ν	$0.09 \pm < 0.01$
Total S [g kg ⁻¹ DM]	0.28 ± 0.02	Р	0.35 ± 0.01
P available [mg kg ⁻¹ DM]	48.6 ± 1.5	K	0.28 ± 0.01
K available [mg kg ⁻¹ DM]	158.8 ± 5.6	S	67.1 ± 2.4
Mg available [mg kg ⁻¹ DM]	129.1 ± 4.7	Mg	9.28 ± 0.46
Ca exchangeable available [g kg ⁻¹ DM]	2.44 ± 0.08	Ca	1.68 ± 0.07

Table 1. Selected chemical properties of soil and waste used in experiment (average \pm standard error, n = 3).

plant nutrition with sulphur and to recognize the burden to the natural environment, particularly to water resources (Schnug, 1998). Presented experiments aimed at determining the effect of applied mineral fertilizers, waste from magnesium sulphate production and liming on the sulphur content in spring wheat, in soil and in soil effluents.

MATERIAL AND METHODS

The assessment of applied fertilization effect on the plant, soil and sulphur losses due to leaching was conducted in a pot experiment in a wire netting-protected unheated greenhouse, in the pots equipped with the effluent draining systems. The soil material used for the experiments (medium silt loam with 44% granulometric fraction of $\emptyset < 0.02$ mm) was collected from the 0–30 cm of the arable layer. The characteristics of selected chemical properties of the soil material were given in Table 1.

The investigations were conducted for three years (2004–2006) in polyethylene pots, 28 cm in diameter and 38 cm high, containing 22.0 kg of air-dried soil material. The experiment, conducted in three replications and in two series: without liming (0 Ca) and limed (+ Ca), comprised 6 treatments: 0 - soil without fertilizers, NPK – soil fertilized with nitrogen, phosphorus and potassium, NPK + S1 a.s. – soil fertilized with nitrogen, phosphorus, potassium and sulphur supplied as ammonium sulphate, NPK + S1 w. – soil fertilized with the waste from magnesium sulphate production and NPK + S3 a.s. – soil fertilized with nitrogen, phosphorus, potassium and sulphur supplied with the waste from magnesium sulphate production and NPK + S3 a.s. – soil fertilized with nitrogen, phosphorus, potassium and sulphur supplied with the waste from magnesium sulphate production and NPK + S3 a.s. – soil fertilized with nitrogen, phosphorus, potassium and sulphur supplied with the waste from magnesium sulphate production and NPK + S3 a.s. – soil fertilized with nitrogen, phosphorus, potassium and sulphur supplied with the waste from magnesium sulphate production and NPK + S3 a.s. – soil fertilized with nitrogen, phosphorus, potassium and sulphur supplied as ammonium sulphate in a dose three times as high as that introduced to the soil on NPK + S1 a.s. and NPK + S1 w.

Prior to the experiment outset the soil was gradually moistened until 30% of the maximum water capacity. After moistening a part of the soil material was limed, separately in each pot, in order to increase pH value. Liming was applied with chemically pure CaO, in the dose established on the basis of the soil total hydrolytic acidity. Subsequently, soil material without liming as well as limed was left for 4 weeks and water losses were supplemented occasionally. After that time, mineral fertilizers and the waste from magnesium sulphate production were mixed with the soil. The content of dry matter in the analyzed waste was 630 g kg⁻¹ and total nitrogen 0.09 g kg-1 DM. Determined conductivity value was 14.9 mS cm⁻¹. The other chemical properties of the waste were presented in Table 1. The doses of nitrogen, phosphorus and potassium, equal for all treatments, were respectively: 0.14 g N, 0.10 g P and 0.15 g K kg⁻¹ soil DM. Sulphur was used once in the first year of the experiment. The sulphur dose on NPK + S1 a.s. treatments and NPK + S1 w. was 0.04 g S and in the treatment with NPK + S3 a.s. was 0.12 g S kg-1 soil DM. Basic fertilization in the first year of the research on NPK; NPK + S1 a.s.; NPK + S3 a.s. and supplementary on NPK+S1 w. was applied in the form of chemically pure salt solutions, respectively: nitrogen as NH₄NO₃, phosphorus as Ca(H₂PO₄)₂·H₂O and potassium as KCl, whereas sulphur was used as $(NH_4)_2SO_4$. In the second and third year of the research supplementary doses of nitrogen, phosphorus and potassium (identical on all treatments) were applied (0.10 g N; 0.02 g P and 0.14 g K kg⁻¹ soil DM). The elements, like in the first year, were supplied as solutions of chemically pure salts.

Spring wheat, Nawra cv. was cultivated in each year of the experiment. The plant density was 28 pieces per pot. Wheat was harvested at full grain maturity. The length of the growth period was 109 days in the first year, 104 days in the second and 96 days in the third. During the experiment the plants were watered with distilled water to maintain 50% of the soil water capacity.

In order to determine the changes of chemical properties, soil samples for analyses were collected from each pot separately after the completion of vegetation season.

After the harvest, wheat plants were divided into roots, straw and ears. The ears were threshed mechanically to obtain grain biomass. In order to determine dry mass yield, the individual fractions of wheat yield were dried (at 70°C) in a dryer with hot air flow to constant weight. The plant material (separately grains, straw and roots) were crushed in a laboratory mill. After crushing, the plant material was wet mineralized in the concentrated HNO₃ (d = 1.40 g mol⁻¹). After evaporation on a sand bath, the samples were min-

eralized in a muffle furnace, initially at 300°C (for two hours), and subsequently at 450°C (for three hours). The remains were dissolved in diluted HNO₂ 25% (v/v) (Ostrowska et al., 1991).

In the soil material collected from the pots and sifted through a sieve with 1 mm mesh, sulphate sulphur content was assessed after the extraction (30 minutes on a rotor mixer) with 0.03 mol dm⁻³ CH₃COOH solution maintaining the soil to solution ratio 1:10 (Ostrowska et al., 1991). In soil material samples dried at room temperature (c.a. 25°C), ground in a porcelain mortar and sifted through a 1 mm mesh, pH was additionally assessed by potentiometer in the suspension of soil and 1 mol dm-3 KCl solution, maintaining the soil to solution ratio of 1:2.5 (Ostrowska et al., 1991).

During the vegetation period, soil lump in a pot was washed with distilled water at 30-day intervals simulating the 36 mm high rainfall. The obtained soil effluent was collected after each washing and kept in a refrigerator at 4°C. Total sulphur was determined after evaporating 100 cm³ of the soil effluent and dissolving the remains in a diluted nitric acid 1:2 (v/v) (Elbanowska et al., 1999).

The sulphur content in the prepared experimental material (plant, soil and effluent) was assessed by means of ICP-AES method on JY 238 Ultrace apparatus.

The chemical analysis of the plant and soil material, and soil effluents was conducted in three replications. In order to verify the assessment results obtained for the plant material, the initial soil and waste material, plant reference material - NCS DC73348 (China National Analysis Center for Iron & Steel) and soil reference - EnviroMAT, SS-2

 $37.0\pm0.63^{\rm a}$

 $49.2\pm0.86^{\text{b}}$

 67.9 ± 1.30^{cd}

 74.1 ± 1.57^{d}

 70.4 ± 1.99^{d}

0 (without fertilization)

NPK

NPK + S1 a.s.

NPK + S1 w.

NPK + S3 a.s.

(SCP Science) was added to each analyzed series. The result was considered reliable if the relative standard error did not exceed 5%.

The obtained results were elaborated statistically according to the constant model where the factor was fertilization and liming. Two-way ANOVA was used for statistical computations and the significance of differences was estimated by t-Tukey test at significance level $\alpha < 0.01$. The value of correlation coefficient (r) was computed using nonparametric Spearman's rank test for sulphur content in the soil effluents, for plant yields and for sulphate sulphur content in soil. All statistical computations and graphic presentations were conducted using Statistica PL package (Stanisz, 2007).

RESULTS AND DISCUSSION

The greatest diversification in wheat grain yield among the treatments and experimental series was found in the first year of the experiment (Table 2). Despite the fact that the differences were not confirmed statistically, greater yields of wheat grain biomass were harvested in the non-limed series, irrespective of applied fertilization. Introduction of the sulphur dose to the soil which was three times as great as that in the NPK + S1 w. treatments, caused a significant decrease in wheat grain yield, but only in the limed series. In the second and third year of the research, wheat grain yields, independently of the experimental series, were far less diversified among treatments, at levels of yields comparable with those obtained in the first year.

 $2.46\pm0.10^{\text{ab}}$

 $4.60\pm0.35^{\circ}$

 $4.86\pm0.25^{\circ}$

 3.82 ± 0.22^{abc}

 4.08 ± 0.31^{bc}

Treatment –	Grain [g DM pot ⁻¹]		Straw [g DM pot ⁻¹]		Roots [g DM pot ⁻¹]		
	0 Ca	+Ca	0 Ca	+ Ca	0 Ca	+ Ca	
-	1st year						
0 (without fertilization)	$46.1\pm0.96^{\text{ab}}$	$39.4 \pm 1.52^{\mathrm{a}}$	$45.3\pm1.06^{\rm a}$	$47.6\pm2.23^{\rm a}$	$3.23\pm0.23^{\text{abc}}$	$2.32\pm0.14^{\rm a}$	
NPK	$62.8\pm1.32^{\text{cde}}$	$50.1\pm2.15^{\text{ab}}$	$70.1 \pm 1.88^{\text{d}}$	$57.7 \pm 1.79^{\text{b}}$	$4.66\pm0.17^{\circ}$	$2.97\pm0.22^{\rm ab}$	
NPK $+$ S1 a.s.	$65.6 \pm 1.74^{\text{de}}$	55.3 ± 2.14^{bcd}	$69.9 \pm 1.64^{\text{d}}$	62.6 ± 2.14^{bcd}	$4.58\pm0.34^{\rm c}$	3.42 ± 0.25^{abc}	
NPK + S1 w.	$66.4 \pm 1.78^{\text{de}}$	67.5 ± 2.55^{e}	$65.0\pm1.97^{\text{bcd}}$	$61.8\pm2.86^{\text{bcd}}$	$4.46\pm0.34^{\circ}$	3.80 ± 0.36^{abc}	
NPK + S3 a.s.	$63.6\pm2.46^{\text{cde}}$	$52.2\pm2.94^{\rm bc}$	$67.8\pm2.14^{\text{cd}}$	$59.8 \pm 1.19^{\text{bc}}$	$4.62\pm0.31^{\circ}$	$2.89\pm0.18^{\rm a}$	
	2nd year						
0 (without fertilization)	$45.2\pm4.26^{\rm a}$	$46.7\pm1.15^{\text{ab}}$	$35.7\pm0.70^{\rm a}$	$36.3\pm1.06^{\text{a}}$	$2.28\pm0.44^{\rm a}$	$2.25\pm0.19^{\rm a}$	
NPK	$63.0 \pm 1.84^{\circ}$	$60.6 \pm 2.74^{\circ}$	$51.9\pm1.74^{\rm b}$	$50.2\pm1.67^{\rm b}$	$4.27\pm0.37^{\rm bc}$	$4.16\pm0.25^{\rm bc}$	
NPK $+$ S1 a.s.	$67.3 \pm 2.86^{\circ}$	$63.6 \pm 1.81^{\circ}$	$55.2\pm1.22^{\rm b}$	$51.0\pm0.93^{\rm b}$	$4.89\pm0.12^{\circ}$	$3.21\pm0.18^{\rm ab}$	
NPK + S1 w.	$63.3\pm0.90^{\circ}$	$61.1 \pm 2.74^{\circ}$	$54.7\pm1.15^{\mathrm{b}}$	$53.0\pm2.03^{\rm b}$	$3.82\pm0.13^{\rm bc}$	$3.41\pm0.18^{\rm ab}$	
NPK $+$ S3 a.s.	$65.3\pm0.97^{\circ}$	$60.1\pm2.30^{\mathrm{bc}}$	$55.5\pm1.10^{\rm b}$	$51.3\pm2.20^{\rm b}$	$4.16\pm0.18^{\text{b}}$	$3.75\pm0.25^{\rm bc}$	
	3rd year						

Table 2. Yield of dry matter (average \pm standard error, n = 3) of grain, straw and biomass of roots of spring wheat.

 $39.2\pm0.17^{\text{ab}}$

 $62.7\pm1.18^{\circ}$

 $74.4\pm2.53^{\text{d}}$

 $68.3\pm2.75^{\text{cd}}$

 69.6 ± 2.51^{cd}

Values followed by the same letters in columns did not differ significantly at $\alpha < 0.01$ according to the t-Tukey test; factors: fertilization x liming; a.s. - ammonium sulphate, w. - waste.

 35.2 ± 1.15^{a}

 $54.7\pm1.86^{\text{b}}$

 $69.6\pm1.29^{\circ}$

 $67.6 \pm 2.25^{\circ}$

 63.2 ± 2.22^{bc}

 $37.3\pm1.04^{\rm a}$

 $61.2\pm0.92^{\rm bc}$

 $69.0\pm1.30^{\circ}$

 $63.5 \pm 2.60^{\text{bc}}$

 $67.7 \pm 2.69^{\circ}$

 $2.23\pm0.22^{\mathrm{a}}$

 $4.26\pm0.43^{\circ}$

 $4.34\pm0.19^{\rm c}$

 $4.20\pm0.35^{\circ}$

 3.82 ± 0.15^{abc}

Straw biomass yield revealed similar dependencies as wheat grain yield. The greatest yields of straw dry mass were harvested from the non-limed series (0 Ca) in the first year of research, whereas in the limed series (+ Ca) the highest yields were obtained in the third year (Table 2). No apparent decline in yield of straw dry mass was registered on the treatment where sulphur was used in a dose three times as high as that in NPK + S1 a.s. and NPK + S1 w. treatments.

The quantity of wheat root biomass from individual treatments did not differ significantly within the experimental series (0 Ca, + Ca), irrespective of the year (Table 2). Slightly smaller amounts of biomass were obtained from this plant part in the first and second year of the experiment in the limed series treatments (+ Ca) as compared to the analogously fertilized treatments in the non-limed series (0 Ca). Like in the case of wheat grain and straw, but only in the first year of research, markedly smaller amounts of those plant parts were produced in the treatment where a three times higher dose of sulphur was used.

The average (for three years) total yield of spring wheat biomass (grain, straw and roots) at comparable values of the arithmetic mean standard error for individual treatments, was the greatest after the application of sulphur as ammonium sulphate against the background of nitrogen, phosphorus and potassium fertilization (NPK + S1 a.s.) (Figure 1). In comparison with the biomass yield from the treatments where smaller sulphur dose was applied, both as ammonium sulphate (NPK + S1 a.s.) and as the waste from magnesium sulphate production (NPK + S1 w.), a smaller biomass yield was produced in the treatment where sulphur was used in a dose which was three times bigger (NPK + S3 a.s.).

Attempts to increase crop yields are based on the activity of three factor groups: advances in plant breeding (obtaining highly productive cultivars); efficient plant protection and increased fertilizer consumption (Delin et al., 2008). Under the soil and climatic conditions of Poland nitrogen is the fertilizer component which determines the yield and crop quality (Ciećko et al., 2006). However, soil fertility and therefore its fecundity are determined also by the content of bioavailable forms of other nutrients, including sulphur, whereas unbalanced fertilization with this element may prove a burden to the natural environment. Proper plant supply with sulphur influences favourably the photosynthesis process, protein biosynthesis and the content of nucleic acids which results in a suitable technological value of the crop (Luo et al., 2000; Wieser et al., 2004). Despite the fact that wheat belongs to the group of plants with relatively small requirements for this element, at sulphur deficiencies and at high nitrogen doses N:S ratio may be disturbed, which, as a result, may decrease nitrogen utilisation and lead to a decline in yield. Spring wheat fertilization conducted in this experiment both in the form of ammonium sulphate and as the waste

from magnesium sulphate production caused a greater increase in grain biomass in comparison with the amount of this part yield harvested from the treatment where no fertilization with this element was conducted. However, it should be emphasized that such visible plant reaction to fertilization with this element was observed only in the first year of research. It shows that a single application of sulphur fertilization during three years is insufficient to meet the plant nutritional requirements. According to Schnug et al. (1993) the increase in yield in the treatments where sulphur fertilization was applied might have been caused by a better utilisation of mineral nitrogen by spring wheat as compared with this element utilisation in the treatments where sulphur was not supplied. The assumed "residual" effect of the applied fertilization with the waste from magnesium sulphate production on plant yielding was not confirmed, either. In comparison with the NPK + S1 a.s. and NPK + S1 w. treatments, an addition of a thrice larger sulphur dose to the soil on NPK + S3 a.s. treatment caused a decline in wheat grain yield, mainly in the first year of the experiment, however, it indicates the necessity of plant fertilization with sulphur strictly following the requirement for this element. Skwierawska et al. (2008) also demonstrated that larger sulphur doses, particularly used in the sulphate form caused a reduction of biomass yield, among others in spring barley by additionally limiting the amounts of absorbed potassium. According to Brodowska (2003), apart from sulphur fertilization, also soil liming has a major influence on growth and development of wheat plants. In the experiments of this study smaller wheat biomass yields were obtained from limed soil. It might have been due to too short a period of time which elapsed from the liming to seed sowing. In consequence it caused negative wheat response to this measure, mainly in the first year of the research.

The average weighed content of sulphur in grain, straw and roots of wheat from the treatment where sulphur was supplied was significantly greater than the content assessed in wheat biomass which was not fertilized with this element (Table 3). In comparison with the sulphur content determined in wheat aboveground parts in the treatment unfertilized with sulphur (NPK) the increase in this element content, regardless of the experimental series, was for grain: 9% in the NPK + S1 a.s. treatment, 14% in NPK + S1 w. and 13% in NPK + S3 a.s., whereas for straw respectively 30%, 38% and 48%. On the unfertilized treatments the mean weighed sulphur content was significantly higher than that determined in the treatments without sulphur supplement (NPK), which in this case resulted from the cumulation of this element in a smaller crop.

The amounts of sulphur uptake with spring wheat biomass yield were over 30% higher (averaged over years, treatments and series) in the treatments where sulphur fertilization was applied in comparison with quantities of this element taken up by plants in the treatments where wheat



Fig. 1. Average (from three years) biomass yield (Σ yields of grain, straw and roots) of spring wheat.



a.s. - ammonium sulphate, w. - waste

Fig. 2. Sulphur uptake (Σ from three years) with biomass yield of spring wheat

was fertilized only with nitrogen, phosphorus and potassium (NPK) (Figure 2). Analyzing the effect of liming on the amounts of sulphur taken up with wheat biomass yield, it was found that slightly bigger quantities of this element were absorbed from the non-limed soil (0 Ca), irrespectively of the applied fertilization.

According to Kaczor et al. (2004) sulphur concentrations in plants are conditioned, beside fertilization, by plant development stage and plant organ, but also depend on soil liming. In the conducted experiment the weighed mean-based sulphur content in grains, straw and roots of wheat fertilized with sulphur was significantly higher than that assessed in biomass of wheat non-fertilized with this element. An increase in the sulphur content in plant biomass as a result of fertilization was also noted by McGrath

Table 3. Average weighted content from three years (average \pm standard error, n = 9) of sulphur in dry matter of grain, straw and roots of spring wheat.

0 Ca	+ Ca	
Grain [g S kg ⁻¹ DM]		
$1.22\pm0.03^{\rm a}$	$1.31\pm0.03^{\text{ab}}$	
$1.32\pm0.03^{\rm ab}$	$1.45\pm0.06^{\rm bc}$	
$1.44\pm0.04^{\circ}$	$1.57\pm0.07^{\rm c}$	
$1.56\pm0.01^{\circ}$	$1.60\pm0.02^{\rm c}$	
$1.55\pm0.07^{\circ}$	$1.58\pm0.04^{\rm c}$	
Straw [g S kg ⁻¹ DM]		
$2.24\pm0.10^{\rm bcd}$	$2.31\pm0.06^{\text{bcd}}$	
$1.61\pm0.03^{\text{a}}$	$1.57\pm0.04^{\rm a}$	
$2.08\pm0.06^{\rm bc}$	$2.06\pm0.01^{\text{b}}$	
$2.18\pm0.07^{\rm bcd}$	$2.21\pm0.02^{\text{bcd}}$	
$2.38\pm0.07^{\rm d}$	$2.32\pm0.05^{\text{cd}}$	
Roots [g S kg ⁻¹ DM]		
$1.58\pm0.19^{\rm b}$	$1.42\pm0.05^{\rm b}$	
1.22 ± 0.11^{a}	$1.42\pm0.21^{\rm b}$	
$1.43\pm0.11^{\text{b}}$	$1.43\pm0.17^{\rm b}$	
$1.30\pm0.03^{\rm a}$	$1.51\pm0.19^{\rm b}$	
$1.52\pm0.24^{\rm b}$	$2.01\pm0.11^{\rm b}$	
	$\begin{array}{c} 0 \text{ Ca} \\ & \text{Grain [g S} \\ 1.22 \pm 0.03^{a} \\ 1.32 \pm 0.03^{ab} \\ 1.32 \pm 0.03^{ab} \\ 1.44 \pm 0.04^{c} \\ 1.56 \pm 0.01^{c} \\ 1.55 \pm 0.07^{c} \\ & \text{Straw [g S} \\ 2.24 \pm 0.10^{bcd} \\ 1.61 \pm 0.03^{a} \\ 2.08 \pm 0.06^{bc} \\ 2.18 \pm 0.07^{bcd} \\ 2.38 \pm 0.07^{d} \\ & \text{Roots [g S} \\ 1.58 \pm 0.19^{b} \\ 1.22 \pm 0.11^{a} \\ 1.43 \pm 0.11^{b} \\ 1.30 \pm 0.03^{a} \\ 1.52 \pm 0.24^{b} \end{array}$	

Values followed by the same letters in columns did not differ significantly at $\alpha < 0.01$ according to the t-Tukey test; factors: fertilization x liming; a.s. - ammonium sulphate, w. - waste.

et al. (1996), Zhao et al. 1996 and by Haneklaus and Schnug (1992). Also Shahsavani and Gholami (2008) observed an increase in sulphur content in various spring wheat cultivars as a result of applied fertilization with this element, moreover, they demonstrated highly significant relationship between the sulphur content and protein concentrations in grain. In term of crop quality, the content and quality of protein are more important than the sulphur content. At proper plant supply with sulphur, changes occur in the initial period of seed development, which results in the increase in the level of protein accumulation. It has been reported for some time that in wheat exposed to sulphur deficiencies, protein nitrogen constituted less than 25% of the total nitrogen content in plant, whereas under conditions of optimal plant nutrition with this element about 75% of nitrogen was built in the protein. Sulphur supplement to the soil causes lowering the value of the ratio of total nitrogen to total sulphur, at the same time increasing the value of the ratio of protein nitrogen to sulphur contained in protein compounds. Despite thrice larger sulphur dose supplied to the soil in the NPK + S3 a.s. treatment in comparison with NPK + S1 a.s. and NPK + S1 w. treatments concentrations of this element in wheat biomass did not differ significantly from the content found in the plant biomass from other treatments



Fig. 3. Value pH_{KCl} of soil.

fertilized with sulphur. It shows that despite considerable content of bioavailable forms of this element in soil, wheat plants were not taking it up in excess. It might be supposed that choosing a more sulphur-demanding plant for cultivation might lead to greater accumulation of this element in plant biomass (McGrath and Zhao, 1996; Kaczor et al., 2004). According to Ashok and Kumar (2008) the content of sulphur and the amount thereof absorbed by plants are most strongly affected by the soil abundance in this element. According to Nesheim et al. (1997) the form in which sulphur was supplied to the soil is equally important.

Regardless of the experimental series (0 Ca or + Ca) or the year of research the lowest pH values were assessed in the soil from treatments fertilized with nitrogen, phosphorus, potassium and a triple dose of sulphur (NPK + S3 a.s.) (Fig. 3). Statistical analysis of the results confirmed a significantly better effect of mineral fertilization with nitrogen, phosphorus and potassium and with the waste from magnesium sulphate production (NPK + S1 w.) on this parameter value in comparison with the soil from the other fertilizer treatments, regardless of the experimental series (0 Ca, + Ca). However, it should be emphasized that liming obviously decreased the rate of soil acidification process.

Fertilization with S markedly affected the sulphate sulphur content in soil (Fig. 4). The greatest amounts of sulphate sulphur, regardless of the experiment series (0 Ca or + Ca) were determined in the soil from the treatment where thrice bigger dose of this element was used (NPK + S3 a.s.). Much smaller sulphur quantities were assessed in the soil from both experimental series in the treatments where smaller sulphur dose was supplied both as ammonium sulphate (NPK + S1 a.s.) and as the waste from magnesium sulphate production (NPK + S1 w.). The contents of these sulphur forms in soil decreased in both limed and non-limed soil in the second and third year of the research in all treatments where this element was supplied with fertilizers. In the soil from the treatments where lower sulphur dose was used (NPK + S1 a.s. and NPK + S1 w.) and irrespectively of the experimental series, after three years of the experiment the content of sulphate sulphur was on the level found in the soil of treatments where solely nitrogen, phosphorus and potassium (NPK) fertilization was applied.

According to Deubel et al. (2007) big doses of sulphur do not worsen the conditions of plant growth, however, fertilization despite its favourable effect, is an intrusion in the naturally shaped relationship, which once disturbed creates disadvantageous conditions for growth and development of plants, particularly at non-balanced component doses. The obtained results concerning the soil pH most clearly point to unfavourable effect of mineral fertilization on this indicator of soil fertility (Gondek, Kopeć, 2008).

In authors' investigations an increase in the sulphate sulphur concentration in soil resulted from introducing this element with fertilizers. A significant effect of fertilization with these organic materials on the content of bioavailable sulphur was demonstrated by the results of research conducted by Kanal (2001). A single soil fertilization with smaller doses of sulphur, either as ammonium sulphate or as waste from magnesium sulphate production did not produce any durable fertilizer effect, which resulted from sulphur being taken up with crop yield and leached from soil. According to Kozłowska-Strawska and Kaczor (2004) the sulphate sulphur content in soil is not conditioned only by this element dose or the form in which sulphur was supplied to the soil. The content of sulphur mineral forms in soil is among others affected by the plant species but particularly by nutritional requirements of plants concerning sulphur and quantities of sulphur originating from mineralization of soil organic matter (Hu et al., 2002). Ashok and Kumar (2008) demonstrated that sulphur fertilization improved the content of bioavailable forms of this element in soil. Also Wołoszyk (2003) at joint application of compost and industrial waste as phosphogypsum and a mixture of iron (II) sulphate (VI) 7-hydrate for soil fertilization obtained an increase not only in sulphur total forms but also in its sulphate forms in soil.

The content of total sulphur in soil effluents was the highest (regardless of the experimental series 0 Ca or + Ca) in the treatments fertilized with a triple dose of this element in the form of ammonium sulphate (NPK + S3 a.s.) (Fig. 5). Beside the effluents from the non-fertilized treatments, the smallest amounts of sulphur were



a.s. - ammonium sulphate, w. - waste

Fig. 4. Content of sulphate sulphur in soil.



a.s. - ammonium sulphate, w. - waste

Fig. 5. Content of total sulphur in soil effluents.

found in the effluents from treatments receiving mineral fertilization with nitrogen, phosphorus and potassium (NPK). Liming generally led to a lesser sulphur leaching in the first year of the research. In the subsequent two years greater quantities of sulphur were assessed in soil effluents from NPK + S1 w. and NPK + S3 a.s. treatments than in the effluents from the analogously fertilized objects in the non-limed series (0 Ca). In comparison with the identical objects of the non-limed series (+ Ca) were higher as follows: from the NPK + S1 a.s. and NPK + S1 w. on average 25% in the second and 139% in the third year whereas from the NPK + S3 a.s. 22% in the second and 12% in the third year

of the experiment. Total sulphur content in soil effluents was most strongly correlated with sulphate form of this element in soil (r = + 0.816; $\alpha < 0.001$). Much weaker, though significant relationship was registered between sulphur content in soil effluents and spring wheat biomass yield (r = + 0.313; $\alpha < 0.01$).

Apart from unfavourable effect concerning the biological value of the crop biomass, unbalanced fertilization has also a significant influence on the environment. Too large acumulation of fertilizer components in soil not utilized by plants, often leads to their loss through leaching. Therefore, big yields of biomass should not be the only indicator of efficient management of biogenic components. Sulphates are relatively easily leached from soil (Kopeć et al., 1991). Introduction of this element into the soil either as a mineral fertilizer or in the form of waste from magnesium production, caused an increase in the sulphur content in soil effluents. Quantities of this element in the effluent waters were determined mainly by the amount of sulphur supplied to the soil with fertilizers and to a lesser degree with crop yields. Investigations conducted by Kopeć and Gondek (2002) demonstrated that sulphur leaching from soil is determined by the crop yield and therefore by the quantities of absorbed sulphur depending on the applied fertilization. The research results presented in this paper also point to a significant dependence between wheat biomass yield and sulphur concentrations in soil effluents. On the basis of obtained results no apparent effect of soil liming on changes in sulphur concentrations in soil effluents was noted. According to Kopeć and Gondek (2002) an increase in soil pH caused a release of adsorbed sulphates, thus in conditions of limed soil sulphur bioavailability for plants may increase. Such relationship was not proved in conditions of the presented experiment. On the other hand, this process favours leaching of sulphate ions. Liming also causes changes of soil biological activity, which at increased numbers of microorganisms may determine the rate of organic matter mineralization leading to a release of a greater number of sulphur compounds soluble in the soil solution. According to Guzy and Aksomaitiene (2004), liming causes a decrease in sulphur concentration in soil solution and diminishes the quantity of this element leached from the soil profile.

CONCLUSION

1. The average (for three years) total yield of spring wheat biomass (grains, straw and roots), at comparable values of statistical mean standard error for years and for individual treatments, was the greatest after application of sulphur in the form of ammonium sulphate against the background of nitrogen, phosphorus and potassium fertilization.

2. In comparison with biomass yield from the treatments where a lower sulphur dose was used, both as ammonium sulphate and as the waste from magnesium sulphate production, a smaller biomass yield was obtained in the treatment where sulphur was applied in a thrice bigger dose.

3. The mean weighed average sulphur content in grains, straw and roots of wheat fertilized with sulphur was significantly greater than the content determined in the wheat biomass non-fertilized with this element. Increasing sulphur doses did not cause any significant differences in this element concentrations in wheat biomass.

4. A single soil fertilization with smaller doses of sulphur, either as ammonium sulphate or the waste from magnesium sulphate production did not cause any durable fertilizer effect which resulted from sulphur uptake with yield and its leaching from soil.

5. Sulphur fertilization, both in the form of ammonium sulphate and as the waste from magnesium sulphate production, led to increased sulphur concentrations in soil effluents. Amounts of this element in the effluent waters were conditioned mainly by the amount of sulphur supplied to the soil with fertilization but to a lesser degree by crop yields.

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